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Impact of Anionic and Cationic Surfactants Interfacial Tension on the Oil Recovery Enhancement

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Abstract

In this paper, a cationic surfactant of Cetyl trimethyl ammonium bromide and an anionic surfactant of linear alkylbenzene sulfonic acid were used to consider their effect on the interfacial tension and oil recovery factor. According to the results of this study, the anionic surfactant of linear alkylbenzene sulfonic acid has the highest recovery factor of 70%, and cationic surfactant of Cetyl trimethyl ammonium bromide has the second-highest oil recovery factor of about 55%. Therefore, the addition of surfactants due to its beneficial impact on the interface adsorption between oil and water would be an essential point on the oil recovery enhancement. Moreover, the critical micelle concentration value is about 300 ppm and 250 ppm for anionic and cationic surfactants respectively where the two crosslines meet each other and anionic has the highest interfacial tension rather than cationic which has caused to have more oil recovery factor.

Keywords: Interfacial Tension, Critical Micelle Concentration, Surfactant Flooding, Oil Recovery Factor, Capillary Number, Wettability Alteration

1. Introduction

Due to the vitally essential needs of several industries to crude oil for their industrial purposes, petroleum industries have always try to find efficient techniques to enhance oil production rate(Lake et al., 2014; Masnadi et al., 2018; Alipour et al., 2017; Davarpanah et al., 2018). As conventional methods have been weakened bypassing the production time, it is of importance to invent and try novel methods to produce more oil volumes in a cost-efficient way(Patel et al., 2019; Chanioti and Tzia, 2019; Al-Nakhli et al., 2016; Davarpanah et al., 2019). Mobility ratio and capillary number are substantial parameters that considerably influence the enhanced oil recovery processes. Mobility ration reduction and increase of capillary number have caused the lower interfacial tension which considered as one of the crucial parameters on the oil recovery enhancement(Nwidee et al., 2016; Druetta and Picchioni, 2019; Sivasankar and Kumar, 2018; Davarpanah and Mirshekari, 2019c). Chemical flooding, the mixture of technologies as they are more compatible with the reservoir characteristics or regarding their efficiency on special occasions after the secondary recovery methods(Bai et al., 2017; Sun et al., 2018; Guo et al., 2017; Davarpanah, 2018).

Surfactant flooding is considered as one of the efficient chemical enhanced oil recovery techniques in recent decades as it has the potential ability to alter the wettability and reduce the interfacial tension of water-oil. Another reason of using surfactant in oil recovery techniques is related to the low-cost and non-hazardous for the environment(Wang et al., 2017; Lu and Pope, 2017; Alzahid et al., 2019; Davarpanah and Mirshekari, 2019b). In general, surfactants are divided into four main categories of cationic, anionic, amphoteric, and nonionic due to their water dissociation. Regarding the environmental issues and economic aspects of natural surfactants rather than synthetic surfactants, it has widely reported in the literature(Nouqabi et al., 2017; Szaniawska et al., 2017; Rieger, 2017; Davarpanah and Mirshekari, 2019a).

USBM and Amott techniques have been used for several years to measure the wettability alteration in carbonate rocks as they are concentrated on the wettability state alteration. Therefore, wettability alteration is one of the substantial and unique for each reservoir (Okasha et al., 2007). Seethepalli et al. (2004) proposed an investigation on the anionic surfactants on the wettability alteration of carbonate rocks. They conducted some experiments on the interfacial tension, phase behaviour, wettability alteration, and adsorption for anionic surfactants. Therefore, anionic surfactants can change the wettability state of calcite surfaces from oil-wet to water-wet. Its performance was better than cationic surfactants (Seethepalli et al., 2004). According to the experimental evaluation of Jackson and Vinogradov (2012) on the profound impact of wettability alteration in carbonate reservoirs, they used potential streaming measurements to predict the core samples wettability, and it could change the wetting states (oil-wet, water-wet) and surface charges. They concluded that regarding the excess charge that is transported by the brine flow, the significant contrast was investigated between non-aged and aged samples (Jackson and Vinogradov, 2012). Smart water injection in order to enhance oil recovery regarding the ionic composition and desired salinity ranges for different salts is of importance. Alghamdi et al. (2019) investigated the synergistic effects of several brines to predict the wettability alteration state in carbonate reservoirs. They concluded that Na_2SO_4 is strongly recommended for wettability alteration on carbonate reservoirs (Alghamdi et al., 2019). Mahani et al. (2017) done some experimental investigation on the effect of temperature on the wettability alteration in carbonate reservoirs. They investigated dolomite and limestone core samples in different salinities and reservoir estimation temperature. They showed that dolomite has better wettability improvement rather than limestones in high temperature, which is corresponded to their rock type and mineralogy (Mahani et al., 2017).

Kamal et al. (2015) investigated the considerable influence of carboxy betaine surfactant, which is based on the propoxylated anionic and amphoteric surfactant on the increase of the capillary number and interfacial tension decrease. They concluded that anionic surfactant had provided lower interfacial tension rather than amphoteric surfactant. Moreover, they showed that anionic surfactants have higher thermal stability in long term processes (Kamal et al., 2015). Ahmadi et al. (2015) experimentally investigated a new natural surfactant that is extracted from roots of *Glycyrrhiza Glabra* on the oil recovery enhancement as it is low-cost and environmentally-friendly. They concluded that higher concentration of this natural surfactant had caused to more oil recovery factor rather than brine injection (Ahmadi et al., 2015).

We aimed to investigate the considerable influence of a cationic surfactant of Cetyl trimethyl ammonium bromide and an anionic surfactant of linear alkylbenzene sulfonic acid on the interfacial tension and oil recovery factor. Therefore, the addition of surfactants due to its beneficial impact on the interface adsorption between oil and water would be an important point on the oil recovery enhancement as it can increase the oil recovery factor.

2. Materials and Methods

2.1. Materials

In this paper, crude oil was selected from one of the Iranian oilfields in the south-west of Iran. Properties of crude oil that are used in this experiment is statistically depicted in Table 1. To be more reliable, the formation of brine components are the same as reservoir condition with the following composition and salinity as it is statistically explained in Table 2.

Chemicals Formula; in this experiment, a cationic surfactant of Cetyl trimethyl ammonium bromide (henceforth; CTAB) and an anionic surfactant of linear alkylbenzene sulfonic acid (henceforth; LABSA) were used. Cetyltrimethylammonium bromide $[(C_{16}H_{33})N(CH_3)_3Br]$ is a

quaternary ammonium surfactant of the antiseptic cetrimide. Linear alkylbenzene sulfonic acid $[\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{H}]$ is one of the approximately low costs with the greatest synthetic volume of surfactant with the high performance that is dried as the stable powder. Both of the utilized surfactants are compatible with the environment due to their straight chains.

2.2. Core flooding apparatus

The components of coreflood apparatus contained core holder which is supplied with the various fluids by displacement pumps that are located in horizontal section, and the core plug is placed through the core holder to allow the fluids at the input or output at determined pressure and temperature, foam generator, and fluid accumulators. The operational temperature, which is used in this experiment is 42 °C to be more adapted with the reservoir circumstances. The schematic of the core flooding setup is shown in Figure 1.

The core flooding procedure is described in more detail in Table 4.

3. Results and Discussion

3.1. Contact angle

Hydrostatic forces, electrostatic forces, and rock morphology are considered as influential parameters in the prediction of wettability changes phenomenon. Therefore, surfactants can change the wettability to water-wet or immediate wet, which helps to mobilize the entrapped oil in the porous media (Standnes and Austad, 2000). To measure contact angle, drop shape analyzer was used by cutting the core samples into small pieces of 3.8 cm in diameter and thickness of 0.2 cm. This operation was done by trimming machine and then to have relatively flat surfaces it was polished by end face grinder. Finally, the contact angle was measured and recorded. To measure

the effect of surfactants, the small pieces were put into crude oil for 14 days, as it needed to be completely oil-wet. It is schematically depicted in Figure 2.

To consider the effect of each surfactant concentration on the contact angle, different concentrations of Cetyl trimethyl ammonium bromide (CTAB) and linear alkylbenzene sulfonic acid (LABSA) were investigated. It is plotted in Figure 3.

As can be seen in Figure 3, the contact angle has been decreased by the increase of surfactant concentration. When there is no surfactant addition, the contact angle is measured approximately 140 °. In the first steps of surfactant addition, the contact angle decrease is prolonged; however, linear alkylbenzene sulfonic acid more intangible to change the wettability rather than the Cetyl trimethyl ammonium bromide.

3.2. Interfacial Tension Measurement

The interfacial tension between water and oil phase would play a substantial role in oil recovery enhancement due to the capillary number increase. Addition of surfactants has caused a dramatic decrease in the interfacial of water-oil. Thereby, the capillary number has increased and has caused to enhance oil mobilization in the porous media. Pendant drop method was used to measure the interfacial tension between the oil and aqueous phase, and the experimental tests were done in the temperature of 25°C. Impact of two surfactants on the interfacial tension had been investigated on different concentration. As it is evident in Figure 4, for two surfactants, due to the increase of surfactant concentration, there was a dramatic decrease on the interfacial tension of water-oil as it is expected that surface-active monomers were adsorbed and it had cause to more oil mobilization in the porous media. In higher surfactant concentrations, interfacial tension value has reached its minimum value. At this point, there were no significant changes in the interfacial tension which is known as critical micelle concentration (henceforth; CMC) which was illustrated by previous

researchers(Shen et al., 2017; Karimi et al., 2012; Hezave et al., 2013). To measure the critical micelle concentration for two surfactants, conductivity method was used. In this experiment, the CMC value is about 300 ppm and 250 ppm for LABSA and CTAB, respectively, where the two crosslines meet each other.

3.3. Oil Recovery

Surfactants regarding their ability to alter the wettability have played a substantial role in the oil mobilization. Figure 5 indicated the oil recovery factor for three different scenarios of water flooding, water-LASBA, and water-CTAB flooding. In the first period of pore volume injection (up to 0.5 pore volume), there is not any significant difference between the three scenarios as the surfactant concentration is not high enough. Since then, it had increased for surfactant scenarios, and water flooding had witnessed a stable pattern after one pore volume injection as the porous media is water-wet, and it had occupied high permeable pores. LASBA has the highest recovery factor of 70%, and CTAB has the second-highest oil recovery factor of about 55%. Therefore, the addition of surfactants due to its beneficial impact on the interface adsorption between oil and water would be an essential point on the oil recovery enhancement as it can increase the oil recovery factor.

4. Conclusions

Surfactants regarding their ability to alter the wettability have played a substantial role in the oil mobilization. The main conclusions of this study are as follows;

- The CMC value is about 300 ppm and 250 ppm for LABSA and CTAB, respectively, where the two crosslines meet each other.
- LASBA has the highest interfacial tension rather than CTAB, which has caused to have more oil recovery factor.

- LASBA has the highest recovery factor of 70%, and CTAB has the second-highest oil recovery factor of about 55%. Therefore, the addition of surfactants due to its beneficial impact on the interface adsorption between oil and water would be an essential point on the oil recovery enhancement as it can increase the oil recovery factor.
- Linear alkyl benzene sulfonic acid (LABSA) more intangible to change the wettability rather than the Cetyl trimethyl ammonium bromide (CTAB).

Conflict of Interest Statement

Funding: There is no financial support to do this experiment.

Conflict of Interest: The authors declare that they have no conflict of interest.

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Tables;

Table 1. Crude oil characteristics in this oilfield

Parameter	Value	Unit
Density of dead oil @ 15°C	0.9513	Kg/L
API Gravity	25	API
Viscosity @ 40 °C	38.51	cSt
Asphaltene content	5.24	% wt
Water Content	0.17	% Volume

Table2. Formation brine components

Brine Type	TDS (mg/L)	pH (25 °C)	pH (85 °C)	Density (25 °C) g/cm ³	Density (85 °C) g/cm ³
KCl	1540	6.6-6.9	6.5-6.8	1-1.0045	0.985-0.99
MgCl ₂	5142	6.8-7.1	6.65-7	0.95-1	0.98-0.985
CaCl ₂	3125	6.7-7.1	6.5-7	1.0002-1.003	0.98-0.985
NaCl	112540	6.21-6.68	6.12-6.53	1-1.0025	0.975-0.98

Crude oil composition is depicted in Table 3.

Table 3. Crude oil Composition

Composition	Mole%	Composition	Mole%
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C₁	20.14	C₈	3.42
C₂	6.59	C₉	4.13
C₃	5.14	C₁₀	3.84
nC₄	1.25	C₁₁	3.85
iC₄	2.96	C₁₂₊	2.4
nC₅	1.54	CO₂	0.84
iC₅	2.36	H₂S	0
C₆	4.52	N₂	0.3
C₇	20.14		

Table 4. Core flooding steps

Steps	Procedure
1	Provided core samples dried at the temperature of 70 °C for four days.
2	Permeameter-Porodimeter device was used to measure the porosity and permeability.
3	Core Samples were placed in the core holder and the confining pressure is 2.1Pa.
4	Core samples were vacuumed to remove the air for 24 hours.
5	0.5 mL/min of crude oil was injected to the core holder to reach the water cut to 1%.
6	The water flooding procedure is done with the flow rate of 0.5 mL/min to establish the residual oil saturation.
7	The specified volume of two surfactants were injected to the core samples on the miscible condition at the flow rate of 0.5 mL/min to reach the water cut of 99%. The working pressure for the supercritical carbon dioxide is 1.8 Pa.

Figures;

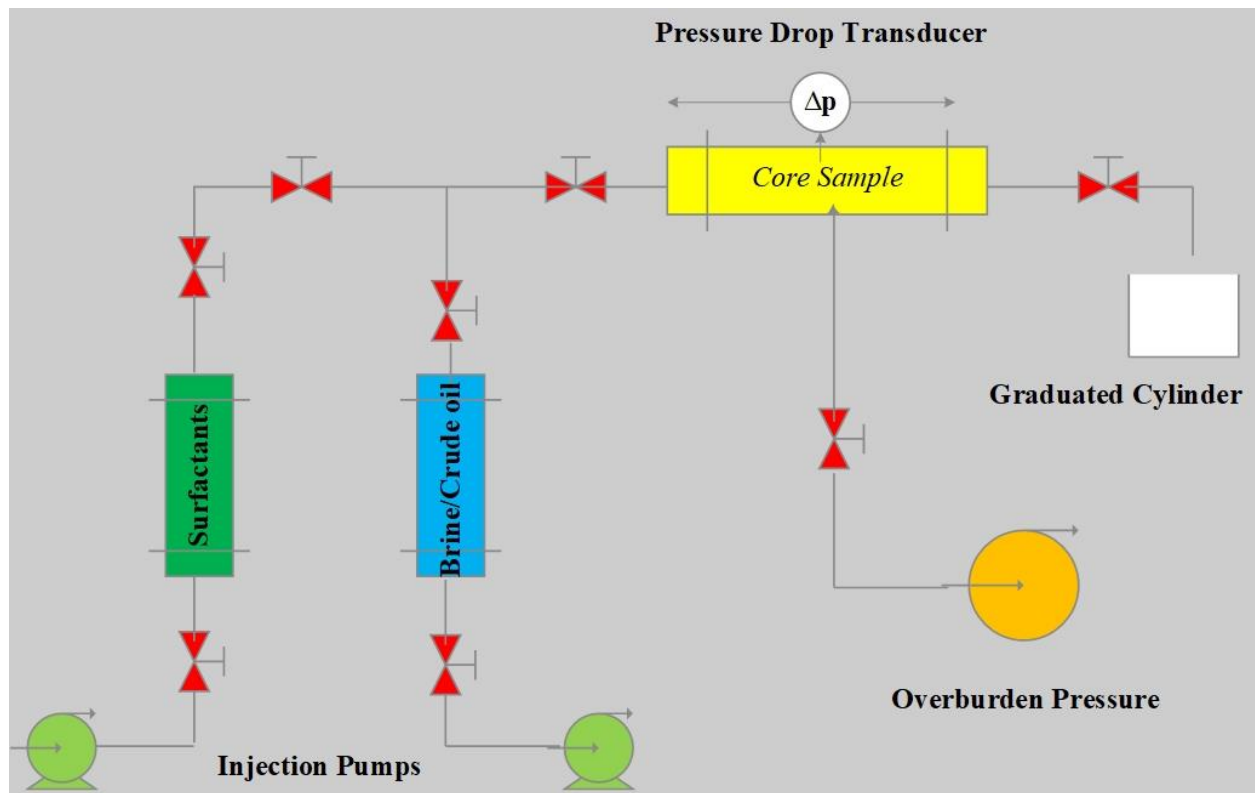


Figure 1. Schematic of coreflooding experiment

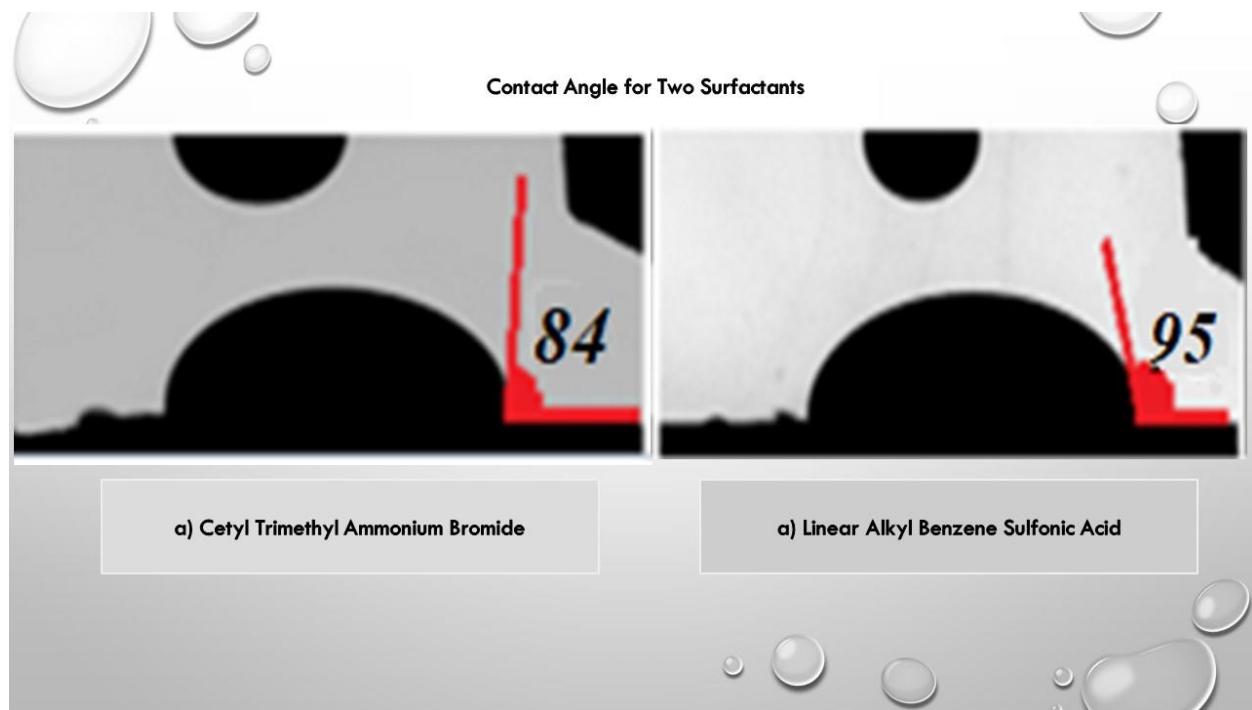


Figure 2. Contact angle for two surfactants

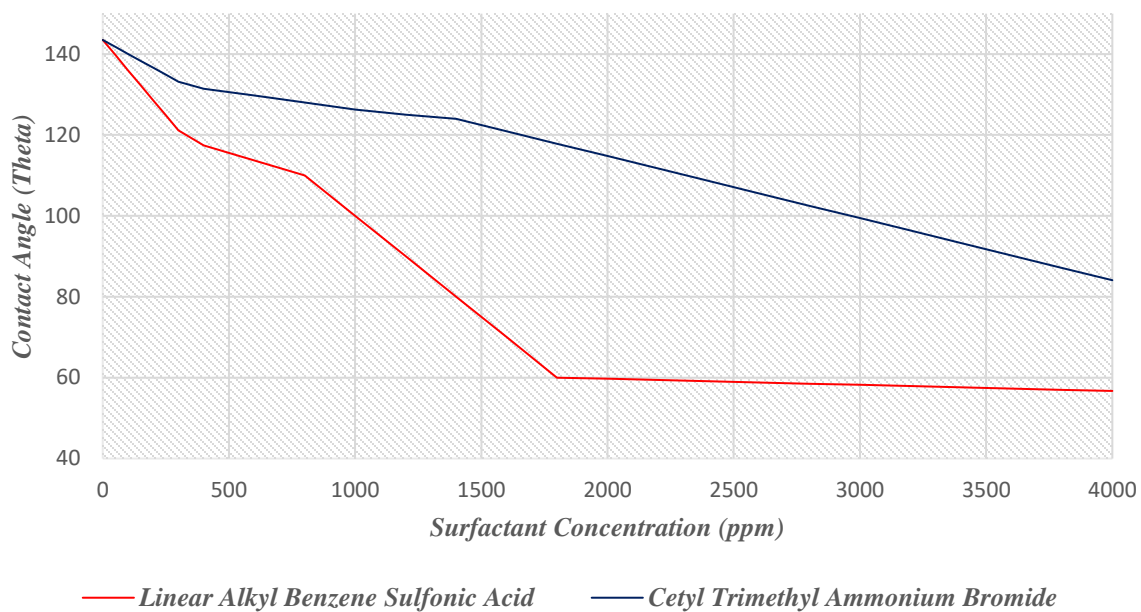


Figure 3. Contact angle measurement for two surfactants.

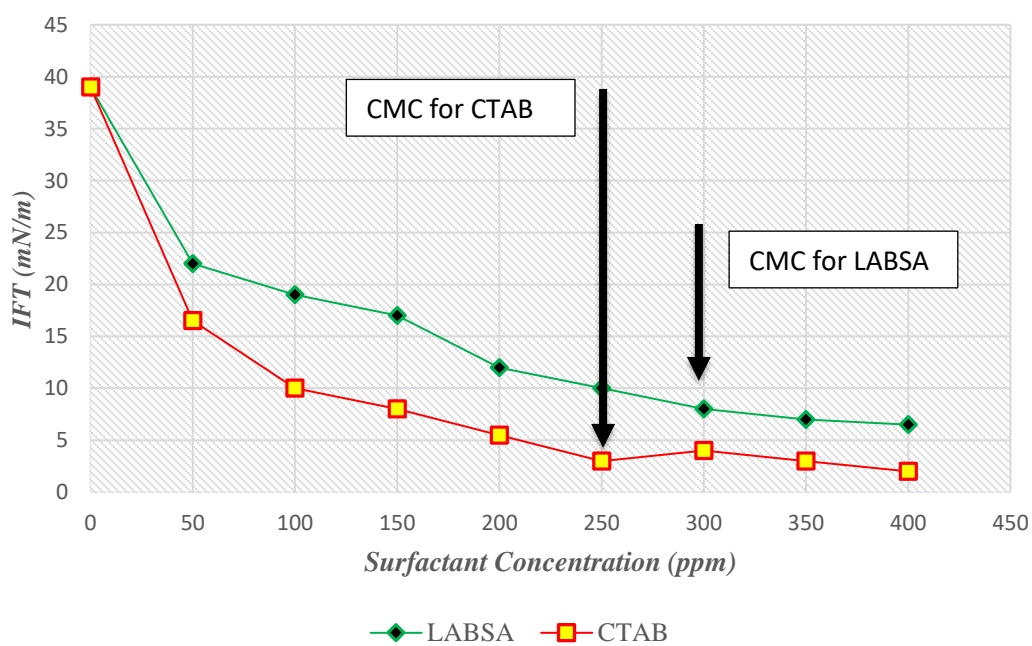


Figure 4. Interfacial Tension for Two Surfactants

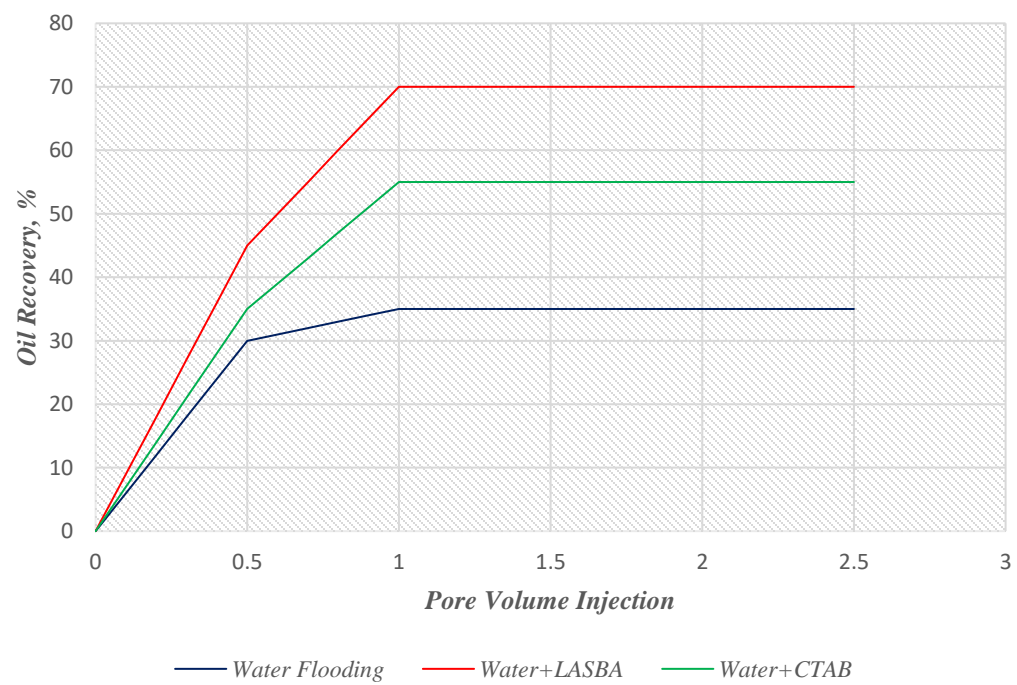


Figure 5. Oil Recovery Factor for different scenarios.